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Nanoscale Metal Powders Production and Applications

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Abstract In this review the methods for production and processing of isolated or agglomerated nanoscale metal particles embedded in organic liquids (nanosuspensions) and polymer matrix composites are elucidated. Emphasis is laid on the techniques of inert gas condensation (IGC) and high pressure sputtering for obtaining highly porous metal powders ("nanopowder") as well as on vacuum evaporation on running liquids for obtaining nanosuspensions. Functional properties and post-processing are outlined in view of applications in the fields of electrically conductive adhesives and anti-microbially active materials for medical articles and consumer goods.

Keywords: nanopowder, nanosuspension, inert gas condensation, conductive adhesives, antibacterial material

1. Introduction

Ultrafine and nanoscale particles have been dealt with in science and technology for more than a century. Aerosil® (SiO_2) and carbon black are the most prominent examples of inorganic nanopowders that are produced on a production scale. But only recently the importance of other type (metal), but similarly structured matter has been acknowledged for various fields of applications, including catalysts, electronics, magnetics, pigments, cosmetics, and medical diagnostics.

In most of these applications well-defined characteristics of the nanoparticles is crucial, like size, shape, coatings, and dispersity. Further, especially in the case of fine particles from ignoble materials it is a challenging issue to ensure a long term chemical and morphological stability under ambient conditions. Stability against oxidation is particularly difficult to achieve for nanoscale metal particles, because of their high chemical affinity to ambient gases. Inorganic or organic coatings are often not applicable, since such coatings often must be removed again in the course of processing. This is one of the reasons, why especially ignoble nanoscale metals are still much less applied than their ceramic counterparts - despite their prospective properties.

Therefore, in general both steps of particle synthesis and processing have to be performed under totally inert or at least reducing conditions.

In this contribution some technological strategies are described for in-situ particle processing to overcome this inherent disadvantage for the preparation of semi-finished products from nanoscale metal particles. Addressed applications include conductive polymers, low temperature bonding and antibacterial materials.

2. Metal Nanopowders from the Gas Phase

There exist two principally different possibilities to synthesize nanosized metal particles from the vapor phase: a) Chemical Vapor Reaction (CVR) of a metal containing precursor gas with a strongly reducing gas, like H_2, and b) Evaporation-condensation of pure metals or alloys in inert carrier gases ("IGC-method"). While in CVR particle formation occurs at high temperatures always the IGC process is running with low temperature cooling gas. Tab. 1 summarises some facts that are typical characteristics for these 2 methods.

2.1. Chemical Vapor Reaction (CVR)

The CVR-method has been developed primarily for the synthesis of nanoscale metal oxide powders, nitrides or carbides, but can also be used for the synthesis of pure and fluffy nanopowders from refractory metals (W, Ta)[10] via reduction of the respective halide gases at high temperature (> 600°C):

Table 1. Gas phase synthesis methods for nanoscale metal particle/powder production: Characteristic product morphology, main advantage vs. main disadvantage of respective method

	Chemical Vapour Reaction (CVR)	Evaporation-condensation (IGC) a) sputtering b) thermal evap.	
Process	gaseous metal-containing precursor in hot wall, flame or arc plasma reactor	magnetron sputtering in inert gas at p > 1 mb, with/without bias	thermal evaporation (Joule/EB/Laser) in inert gas > 5 mb
Morphology	nano-porous powder agglomerates	nano-powder deposits with taylored porosity	nano-porous powder agglomerates
Advantage	high production volume (up to tons/h) many composite material combinations and alloys possible	structured layers (via templates or nozzle)	high purity, no ionic impurities
Disadvantage	residual impurities from gaseous precursor	extremely low volume	low volume

$$TaCl_2 + H_2 \rightarrow Ta + 2\,HCl$$

$$WCl_6 + 3\,H_2 \rightarrow W + 6\,HCl.$$

Inherent limitations are, however, related to the fact that residues of the gaseous halides (mostly Cl) are introduced into the final powder product in the 100 ppm range in general too much for using these powders in corrosion sensitive applications such as in microelectronics. Impurities in nanopowders are hard to remove subsequently: a thermally/chemically induced desorption would inevitably lead to formation of hard aggregates.

In contrast, metal nanopowders that are totally free of ionic impurities (Cl^-, Na^+, K^+, etc.) can be prepared by evaporation-condensation processes in inert gases ("IGC"-methods).

2.2. Inert gas condensation via thermal evaporation (IGC)

This method was first described nearly 70 years ago[13] and is based on the condensation of a supersaturated metal vapor in the presence of an inert gas (e.g. helium or argon). The inert gas acts both as a cooling agent and a carrier gas for the nucleating metal particles. Convection currents established by temperature gradients in the gas chamber can be simulated from first principles.[9] Considering the need for high purity materials especially in microelectronic applications, an intrinsic advantage of the IGC method lies in the fact that absolutely no organic substances or reactive gases are needed for particle formation. Instead the particles are formed by homogeneous nucleation in the inert carrier cooling gas and grow by Brownian coagulation, resulting initially in a coalescence mode of particle growth. As the coalescence mode of particle growth dies out, eventually (but still in the gas flow) these particles form highly porous aggregates with a fractal-like structure and pronounced sinter-necking (for further details of the particle growth mechanism in the gas phase refer to Ref. 5, 3. Processing such powders into "nanostructured" metals by in-situ compaction has first been reported by Ref. 4.

Meanwhile several modifications of the IGC-technology exist such as magnetron sputtering from flat targets or which is much more effective at elevated gas pressures from hollow cathodes. But usually, especially if large powder volumes are needed, the metal is evaporated thermally via Joule, electron beam or laser beam heating from a pool of metal melt that can be fed by a motorised wire-feeder or by a drip-off technique.

At Fraunhofer-IFAM this technology has been developed since 1984 in various variants regarding the principles of both evaporation and collection: Starting from a gas-convection/cold-finger deposition principle combined with a high-voltage electron-beam evaporation, meanwhile Ag nanopowders are routinely prepared in a pilot-scale device using a closed-loop gas flow process (Fig. 1.). For silver a maximum production rate of 250 g/h and a batch size of 5 kg is achieved. In this case the metal melt is continuously fed from a wire reservoir and is evaporated from a Joule-heated tungsten boat at a background pressure (He) above 5 kPa. The powder is deposited on filter bags, removed by a back-flow pressure pulse technique and funnelled into a canning device. Due to the well-pronounced formation of sinter necks in the fluffy network of Ag nanoparticles, a high level of intrinsic dc-conductivity is achieved.

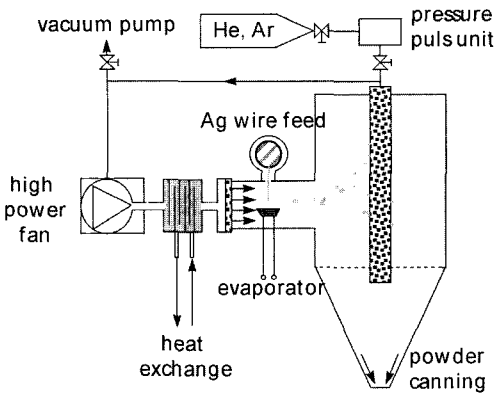

Fig. 1. Schematic principle (left) of the inert gas condensation (IGC) process running as a closed-loop process.[6]

The main impurities in the resulting powder are oxygen (from handling operations under ambient conditions) and 100...500 wt-ppm WO_3 stemming from chemical reaction of the W-evaporator with oxygen that is dissolved in the feeded Ag wire (3N metal purity). Fortunately, this amount can still be tolerated, even if high electrical conductivity of the powder is needed in the respective application.[7] Otherwise, much more expensive, but high-purity oxygen-free starting material had to be used (OFHC-Ag).

2.3. Processing of metal nanopowders

Gas phase produced metal nanopowders (CVR or IGC) are prospective filler materials in polymer matrix composites. Finding the most effective method for dispersing and compounding are important issues. Gas phase produced nanopowders typically consist of soft agglomerates that can be easily dispersed in a carrier liquid down to sub-μm aggregate sizes.

Depending on the shear strength to be introduced into the suspension, various methods exist, such as dissolver, ultrasonic agitator, bead milling, 3-roll-milling, ultra-turrax, and others. In all these methods for preparing metal nanosuspensions and pastes, it is important to infiltrate the dry nanopowder with the carrier liquid before starting the dispersion process. Otherwise the fragile structures would be partially compacted resulting in a structure that is subsequently much more difficult to be dispersed.

2.4. In-situ variants of the inert gas condensation principle(synthesis/processing)

It should be noted that there also exist direct methods for processing as-synthesized metal nanoparticles (skipping the step of agglomeration in the gas phase). One of these "in-situ-methods" is the deposition of thermally evaporated metals onto a liquid substrate[12] resulting in metal nanosuspensions (inks). We have picked up and modified this technology by introducing magnetron sputtering, which is very versatile regarding the type of nanoparticle material to be dispersed in the desired suspension. Depending on the sputtering gas pressure two processes for particle formation may occur: at "high" pressures (mean free path of sputtered atoms larger than the target-substrate-distance L) the sputtered atoms are forming nanoparticles already in the gas phase. At "low" pressures atoms are deposited on the liquid film forming particles by the island growth mechanism that are subsequently dispersed into the liquid. At L = 10 cm the transition gas(Ar)-pressure between these two regimes is around 0.01 mb. This technology can applied only for carrier liquids with a low enough vapor pressure ($< 10^{-3}$ mb) and viscosity (< 1 Pas) at the processing temperature.

Many more chemical technologies exist that are best suited in all those cases, where isolated metal nanoparticles (chemically stabilised by organic/inorganic coating) with a narrow size distribution are needed. Most of these methods are based on the chemical reduction of a metal containing precursor in a polar solvent (polyol-process). A nice and illustrative review on metal nanosuspensions prepared by the polyol processes has recently be given by Ref. 2.

Another interesting variant of the IGC-process is the gas deposition technique developed by Hayashi and Oda[8] : Metal particles that have condensated in high pressure (ca. 4 bar) inert gas are carried through a pipe to a deposition chamber held at low pressure (< 0.1 mb). The high particle speed at the nozzle of more than 1 km/s leads for the resulting films to adhesion strengths that are comparable to those obtained in respective PVD-films. Scanning the substrate against the nozzle allows "writing" of < 50 μm narrow conduction lines.

A similar technique aims at narrow conduction lines, e.g. on printed circuit boards (PCBs) and uses highly focused laser heating of the as-deposited nano particles to sinter the nanoparticle deposit directly after particle deposition.

Another variant of the IGC-method makes use of the sputtering technique, which is capable of producing thin nanoporous deposits that can be processed by in-situ compaction.[11] By varying the pressure of the sputtering

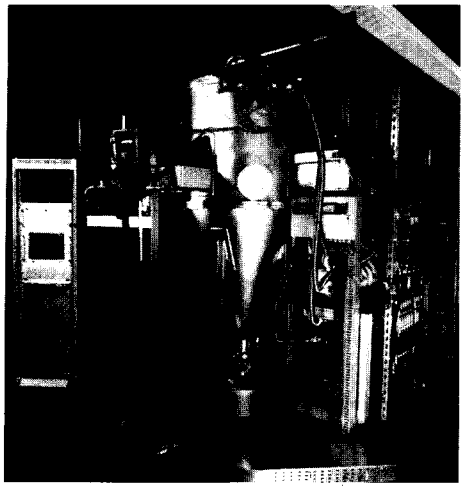

Fig. 2. Pilot-scale production device for Ag-nanopowders with a capacity of max. 1 t/y.

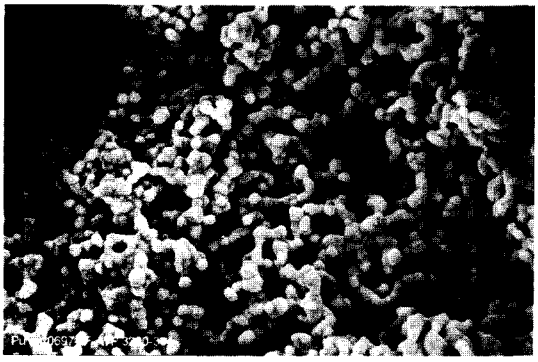

Fig. 3. Typical morphology of a Ag-nanopowder prepared by the high-rate IGC-process. Pronounced sinter neck growth occurs due to the high purity of the metal powder surfaces. The primary particle size is about 100 nm.

gas (Ar) it is possible to taylor the structure of the deposit: The porosity ranges from fully dense at low pressure to highly porous at pressures >0.1 mb. Fig. 4 shows the essential steps of this process that can be usefully applied to pressure-bond 2 substrates e.g. Si

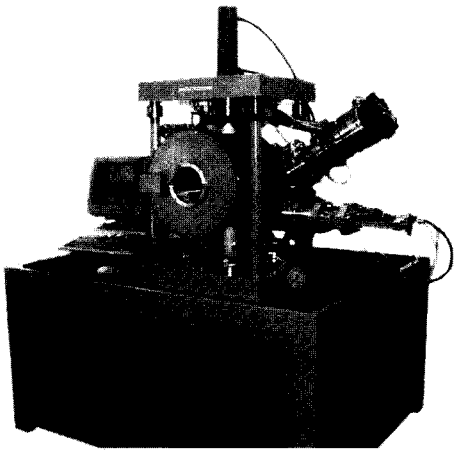

Fig. 5. Demonstrator device for low temperature bonding by sputtered nanopowders.

to Mo heat sink. Due to the clean surface of the in-situ processed metal particles sintering occurs at fairly low temperature for Au even at room temperature. Fig. 5 shows a demonstrator device that puts this idea into practice. Fig. 6. reveals the nearly full density achieved in a gold nanopowder compact sandwiched between two silicon wafer substrates. In tensile tests an adhesion strength of 20 MPa has been achieved at room temperature.

Finally, dispersing metal nanoparticles into thin polymer films can be also achieved by injecting IGC produced metal nanoparticles into a plasma polymerisation process.[14]

All these examples illustrate that in-situ technologies for synthesis/processing metal nanoparticles open up many new possibilities and are particularly useful for realising thin functional coatings and structured layers.

3. Properties and Applications

3.1. Properties of metal nanopowders and composites

In contrast to other methods for gas phase synthesis

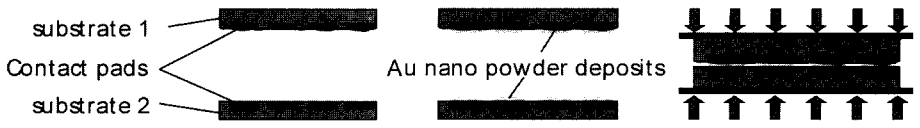

Fig. 4. Process of low temperature metal bonding by using sputtered Au nanopowder deposits: deposit that levels out small surface roughness of the substrate. In a final step the substrates are pressurised.

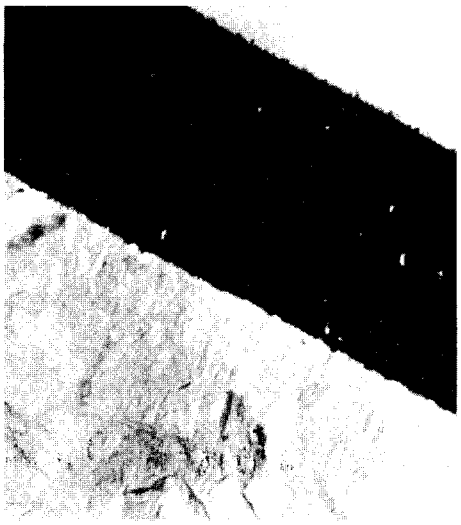

Fig. 6. Compacted Au nanopowder interlayer (thickness 2 μm).

of metal nanopowders from precursor gases, the evaporation/condensation process is a chemically clean process. The only contaminant that may be introduced into the powder as an impurity is the evaporator material itself (typically W, Ta, and Mo). The resulting impurity concentration depends on the amount of residual oxygen in the process gas and the amount of oxygen dissolved in the feeded starting material. As an example in silver powder produced in our high-rate-IGC process typically 100...400 wt-ppm W are introduced as WO_3 formed via an oxidation/sublimation process at the glowing W-evaporator. Fortunately, this amount of WO_3 does not have a detrimental effect on the powder property (conductivity, mechanical property) needed in the applications described below.

In general, nanoscale metal powders produced from the gas phase are agglomerated to some degree. The potential applications of gas-phase-produced metal nanopowders are thus closely coupled to the ability to tailor not only the size of the constituent particles but also the properties of the aggregates. Here the porosity is most important and can be estimated as follows: The bulk powder density can be related to the internal porosity $0 < p_{int} < 1$ of the agglomerate structure and the open volume between the agglomerates (p_{ext}).

$$\rho_{powder} = \rho_{Ag} (1 \; p_{tot})$$

$$p_{tot} = p_{ext} + p_{int} (1 \; p_{ext})$$ or after re-arranging:

$$p_{ext} = (p_{tot} \; p_{int})/(1 \; p_{int}).$$

From TEM-images of ultrathin (40 nm) slices of monomer-infiltrated and cured IGC-agglomerates (primary Ag particle size = 100 nm), one can estimate a value for $p_{int} = 0.6$ (±0.1). Together with a measured tap density of $\rho_{powder} = 0.5$ g/cc one obtains $p_{ext} = 0.88$ (+0.02/-0.04). This large external porosity results from the irregular (fractal) structure of the agglomerates (the same effect makes aerosil® (gas phase produced SiO_2) an extremely high-volume low-weight material). For comparison, modelling a statistically arranged ensemble of monodispersed spherical particles results in $p_{ext} = 0.40$.

In some applications it is necessary to disperse the fluffy powder to some extent, while keeping the highly porous structure intact e.g. in electrically conductive polymer matrix composites. This can be achieved to a certain extent by means of air-jet sieving or related powder technologies, resulting in highly porous powders with an agglomerate size < 10 μm. These can be infiltrated with a liquid resin followed by a compounding step. The introduced shear forces must be high enough to disperse the powder into small enough - but still porous - fragments.

3.2. Applications of metal nanopowders

The following examples should illustrate the prospective applications for metal nanopowders. Metal nanopowders/-particles are particularly interesting as fillers in polymer matrix composites (PMCs), such as electrically conductive adhesives with improved thermomechanical properties needed in surface mounting technology (SMT) or anti-microbially active PMCs. Noble metal nanopowders may also be used as sintering additives in electronic pastes that develop high conductivity during firing at strongly reduced sintering temperature as compared to using no such additive.

3.2.1. Nanocomposites for electrically conductive adhesive bonding

There are basically two effects related to particulate metals in PMC material: Above the percolation threshold limit the electrical conductivity increases as a function of filler content. At the same time the metal filler has an embrittling effect on the composite. This is particularly critical under thermal cycling condition: fatigue effects at the metal polymer interface may lead to premature failure. Therefore reduction of conductive

filler content in PMCs while keeping the dc-conductivity high is important for many applications. Electrically conductive bonding of dissimilar materials (like polymer-to-silicon), e.g. on flexible polymer substrates,

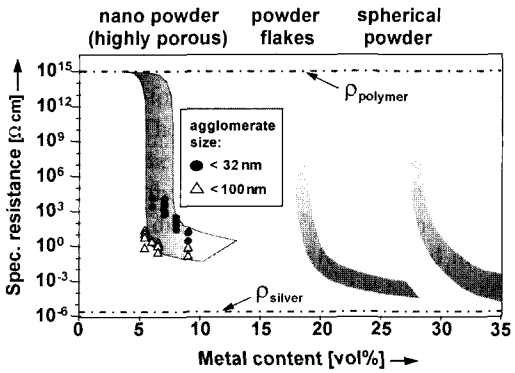

Fig. 7. Specific electrical resistivity of epoxy-based PMCs as a function of filler content for three different powder morphologies. Two sizes of sieved material have been introduced into the PMC.[6)]

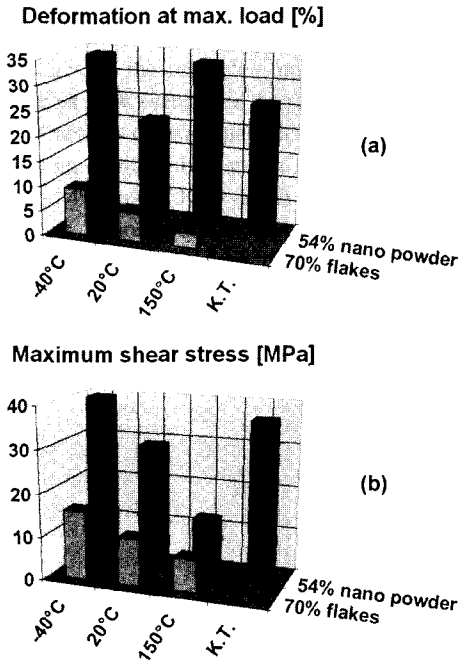

Fig. 8. Thermomechanical properties of cured epoxy composites filled with fine silver flakes (70 wt%) and with Ag-nanopowder (54 wt%). Both the strength and the elongation at the maximum strength are drastically enhanced in the nanopowder composites.

is one such example. We have tested Ag-nanopowders produced via high-rate IGC in epoxy-based adhesives. As expected we found a strong decrease of metal filler content (wt%) at the percolation threshold, if porous Ag-filler from IGC-nanopowder are used instead of the commercially available flake powder (Fig. 7.). This enables the reduction of the filler content while keeping the electrical conductivity high. As a consequence for bondings made with this epoxy/nanopowder adhesive, the mechanical properties under shear stress loading (ISO11003-2) are strongly improved (Fig. 8.) due to this combined effect of a lower content and the open-porous structure of the filler.

3.2.2. Anti-bacterial materials

It is well-known that extremely low concentration of heavy metal ions may inhibit the proliferation of bacteria on material surfaces. In the case of Cu^{2+} and Ag^{+} this can be achieved at concentrations as low as 10^{-6} mole/l (This is why $CuSO_4$-based solutions are often used to prevent microbial growth on plants). Fortunately, silver and copper are non-toxic to human tissue in contrast to most other types of heavy metal ions. This effect can be used to make polymers bacteriostatic by using highly dispersed Ag-/Cu particles at concentrations far below 0.1 vol%. Fig. 9 demonstrates the bacteriostatic effect of a polyvinylchloride (PVC) sample filled with different amounts of Ag nanoparticles. Many other demonstrator parts have been tested revealing the potential of nano-dispersed Ag as a non-toxic non-antibiotic agent that prevents

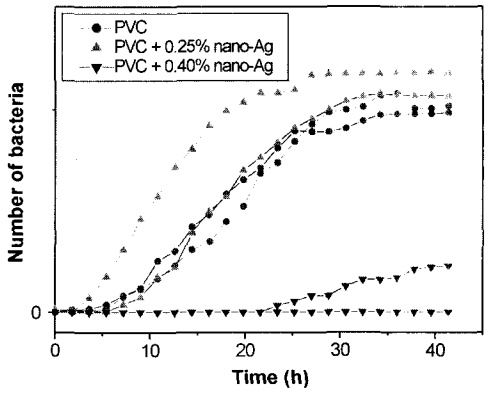

Fig. 9. Number of bacteria counted on the surface of Ag/PVC-matrix composites as a function of time. The composites are filled with different amounts of IGC nanopowder.

microbial growth. Applications are basically in clinical environment and packaging of perishable food.

3.2.3. Sintering additives for electronic paste formulation

Some of the earlier ideas for application of metal nanoparticles is based on the fact that such high specific surface area powder translates to strongly reduced sinter temperatures. This is particularly useful, if conduction leads and pads are needed on polymer substrates in PCB technologies. Here thick film technology can be used provided the sinter temperature can be made low enough. In Ref. 2, it is shown that Ag nanoparticles can be incorporated into a paste of μm-sized particles serving as a sinter-reactive component that allow firing at fairly low temperatures. Specific dc-resistivity values below 1/10 of the bulk silver value have been achieved at a firing temperature as low as 250°C.

4. Summary

Metal nano-powders/-particles embedded in polymer matrix composites (PMCs) show a variety of physical properties that are useful in many applications. The required degree of nanopowder dispersion may range from agglomerated to isolated particles.

Agglomerated metal nanopowder are useful in electrically conductive adhesives, where due to the highly porous structure a drastic shift of the percolation limit for electrical conductivity can be achieved. Powder technology methods can be used to taylor the size of the agglomerate in the composites.

Isolated metal nanoparticles are needed in PMCs, if these particles act e.g., as gas sensitive or superparamagnetic constituent. For realising such composite structures often in-situ technologies integrating both steps of synthesis and processing are a smart solution to many technical problems that exist due to the high chemical and/or catalytic reactivity of metal nanoparticles.

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